CRYSTALLIZATION AND MICROSTRUCTURAL CONTROL OF FERROELECTRIC THIN-FILMS AND GLASS-CERAMICS

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13. ABSTRACT *(Maximum 200 words)*

Research on solution-derived ferroelectric thin-films and melt-derived ferroelectric glass-ceramics was conducted in parallel with considerable overlap in the compositions studied and the evaluations of the crystallization behavior, microstructural development, and resulting properties. Lead germanate based ferroelectric thin films were developed with a room temperature pyroelectric coefficient over 90% of the single crystal value, and a pyroelectric figure of merit exceeding the highest reported value for oriented lead titanate films. New glass-ceramic compositions were developed based on the crystallization of ferroelectric phases of lead zirconate titanate and lead zinc niobate in lead borosilicate glass matrices. The compositions in glass powder form densified at temperatures less than 900°C by a combination of viscous and liquid phase sintering mechanisms. Crystallization of an interconnected microstructure of the ferroelectric phases was critical to produce ferroelectric properties, and allow electrical poling for piezoelectric and pyroelectric activity. This research demonstrates the feasibility of developing ferroelectric glass-ceramic compositions with low processing temperatures that utilize powder processing techniques, such as pressing, screen printing, or tape casting, and indicates the potential incorporation of these materials into multicomponent microelectronic packages as sensors and actuators.

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I. ABSTRACT

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New glass-ceramic compositions were developed based on the crystallization of ferroelectric phases of lead zirconate titanate and lead zinc niobate in lead borosilicate glass matrices. The compositions in glass powder form densified at temperatures less than 900°C by a combination of viscous and liquid phase sintering mechanisms. Crystallization of an interconnected microstructure of the ferroelectric phases was critical to produce ferroelectric properties, and allow electrical poling for piezoelectric and pyroelectric activity. This research demonstrates the feasibility of developing ferroelectric glass-ceramic compositions with low processing temperatures that utilize powder processing techniques, such as pressing, screen printing, or tape casting, and indicates the potential incorporation of these materials into multicomponent microelectronic packages as sensors and actuators.

II. SUMMARY OF THE RESEARCH PROGRAM

A. Introduction

This final report summarizes the activities carried out in the Colorado Center for Advanced Ceramics at the Colorado School of Mines from April 1, 1995 to December 31, 1997 on the ONR sponsored research program, "Crystallization and Microstructural Control of Ferroelectric Thin-Films and Glass-Ceramics." This research program initially began with an ONR Young Investigator Award in 1992. Additional support for this project was provided from an NSF Presidential Young Investigator Award, and from the Colorado School of Mines through significant reduction of overhead charges.

The combined research program resulted in twenty-four publications and manuscripts, eight theses, and thirty-seven invited or contributed presentations as listed in Section III. The research conducted during the continuation phase (April 1, 1995 to December 31, 1997) was divided into the following five projects with at least one graduate student working on each project:

- PZT based Ferroelectric Glass-Ceramics,
- Transient Glass and Liquid Phase Processing of Ferroelectric Ceramics,
- New Ferroelectric Glass-Ceramic Systems,
- Lead Germanate based Ferroelectric Thin-Films, and
- Control of the Densification and Crystallization Behavior of Solution-Derived Ferroelectric Thin Films and Bulk Ceramics.

The following sections briefly describe the significant results that were achieved in each of the five areas of research. Additional details are provided in the references in Section III.

B. PZT based Ferroelectric Glass-Ceramics

Piezoelectric glass-ceramics consisting of PZT crystallites in a lead silicate matrix were developed with the desired combination of glass formability, densification and crystallization behavior, and piezoelectric properties. The effects of Zr/Ti ratio and additions of SrO, MnO_2, Nb_2O_5, and Al_2O_3 were investigated. With these additives the compositions showed similar densification behavior as compositions without additives, however grain growth was inhibited. The PZT grain size of both modified and unmodified compositions were less than 1 μm after heat treatment at 650°C, and increased to 7-8 μm for unmodified and 5-6 μm for modified compositions heat treated at 950°C. The addition of Al_2O_3 increased the glass formability and modified the densification and crystallization behavior. The other additives (SrO, MnO_2, and Nb_2O_5) enhanced the dielectric constant and piezoelectric d_{33} and g_{33} coefficients. MnO_2 and Nb_2O_5 increased the electrical resistivity by about an order of magnitude. The maximum values of dielectric constant and piezoelectric d_{33} coefficient were 137 and 45 pC/N for a composition with all four additives and a Zr/Ti ratio of 50/50. This research demonstrates the feasibility of developing piezoelectric glass-ceramics with low processing temperatures that utilize powder processing techniques, such as pressing, screen printing, or tape casting, and indicates the potential incorporation of these materials into low-fire multilayer packages as sensors and actuators.

C. Transient Glass and Liquid Phase Processing of Ferroelectric Ceramics

A transient glass phase processing method was investigated to increase the PZT content and resulting piezoelectric properties of the PZT glass-ceramics previously developed. Glass compositions in powder form were mixed with crystalline titania and zirconia. By limiting the amounts of these crystalline fillers, the composite mixtures densified by viscous and liquid phase sintering mechanisms. The fillers dissolved into and/or reacted with the glass and/or liquid phases to form additional PZT. An enhancement of the piezoelectric d_{33} coefficient by as much as 35% resulted after firing at the highest temperature of 1050°C. These results demonstrate the potential of enhancing the piezoelectric properties by this transient crystalline filler approach, however higher firing temperatures appear to be necessary.

A similar transient liquid phase processing method was also investigated where low melting (<750°C) lead borosilicate powders were combined with crystalline PZT, titania, and zirconia. By firing above the melting temperature of the lead borosilicate compositions, liquid phase densification occurred followed by dissolution of the titania and zirconia into the liquid phase, and crystallization of additional PZT on cooling. This method was also found to significantly enhance the electrical properties, but again higher firing temperatures were necessary for densification and reaction of the crystalline fillers.

D. New Ferroelectric Glass-Ceramic Systems

Ferroelectric glass-ceramics based on $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), similar to the previously developed PZT glass-ceramics were investigated. The potential of forming PZN glass-ceramics is of particular interest, because single crystal PZN modified with nine mole percent $PbTiO_3$ has the highest known electromechanical coupling factor of 0.92, along with a piezoelectric d_{33} coefficient of 1570 pC/N. PMN and especially PZN are difficult to form into powders and polycrystalline ceramics with the perovskite structure, because of the formation of a nonferroelectric pyrochlore phase.

The glass forming ability of the PZN compositions was significantly greater than that of the PMN compositions, presumably because ZnO is less refractory than MgO. Pyrochlore formation tended to occur in both glass-ceramic systems, but was be controlled through compositional adjustments. Addition of excess PbO combined with reducing the SiO_2/PbO ratio resulted in perovskite formation of up to 92%. The PZN glass-ceramics densified well at 850-950°C, with much higher room temperature dielectric constants (600-800) compared to the PZT glass-ceramics. The PZN glass-ceramics were electrically poled with piezoelectric d_{33} coefficients of $\approx$ 60 pC/N, thirty percent higher than that of the PZT glass-ceramics.

E. Lead Germanate Based Ferroelectric Thin-Films

Ferroelectric thin films in the $Pb_5Ge_3O_{11}$ (PG) and $Pb_5Ge_3O_{11}$ - $PbZr_xTi_{1-x}O_3$ (PG-PZT) systems were deposited on (111) platinized silicon substrates, and processed at a variety of heat treatment conditions to characterize the crystallization behavior and electrical properties. Lead germanate films with grain sizes greater than 1 μm had porous microstructures as a result of grain growth. This resulted in electrical shorting of the films after the surface electrode was deposited. The integrity of these large grained films was significantly improved by additional processing steps. Annealing at 760°C (above the melting point) for one minute, after the annealing step for grain growth, promoted improved film density, apparently by allowing material transport through viscous flow mechanisms. The greatest success in terms of ability to make electrical contact was for films fabricated with a "capping" layer of submicron lead germanate at the film surface. Following the annealing step for grain growth, additional layers of lead germanate were deposited and annealed at 450°C. This resulted in submicron sized lead germanate grains that served to fill the voids between the large grains, effectively sealing the surface.

Results on pyroelectric properties indicate the potential of utilizing lead germanate in pyroelectric applications. A room temperature pyroelectric coefficient of 0.89×10^{-8} C/cm^2°C was obtained for films with c-axis orientation and a 5 μm grain size. This value of the pyroelectric coefficient is over 90% of the single crystal value. The pyroelectric figure of merit for these lead germanate thin films exceeded the highest reported value for oriented lead titanate films. The simplicity of obtaining nearly complete orientation of lead germanate could prove to be advantageous over lead titanate. The room temperature pyroelectric figure of merit for lead germanate (3,700 V/cm°C) was over half that of single crystal triglycine sulfate (TGS). The

chemical and electrical stability, as well as the ease of preparation of lead germanate compared to that of TGS offer significant advantages for pyroelectric applications.

F. Control of the Densification and Crystallization Behavior of Solution-Derived Ferroelectric Thin Films and Bulk Ceramics

The effect of additions of silica and lead silicate to sol-gel derived PZT was investigated in both bulk samples and thin films. The compositions studied were similar to the previously developed PZT glass-ceramics. 60 mole % PZT - 40 mole % $PbSiO_3$ in bulk form densified to 91% of the theoretical density when fired at 900°C. The dielectric constant was 305, five times greater than that of the melt derived material of the same composition. The piezoelectric d_{33} charge coefficient was 59 pC/N, 2.5 times greater than the melt derived material. The dielectric breakdown strength was greater than 70 kV/cm for the sol-gel derived material fired at 900°C. This was a significant improvement compared to pure sol-gel derived PZT fired at 1150°C, which had a breakdown strength of 30 kV/cm. The solution derived thin films were highly oriented with the PZT perovskite (111) peak being dominant. This orientation was enhanced with additions of 5 mole % SiO_2 or $PbSiO_3$ compared to pure PZT. The films densified through the elimination of OR and OH groups by condensation reactions in the pores by ≈ 600°C. Above this temperature the thickness of the films did not decrease significantly. This is in contrast to the densification behavior of the sol-gel derived powders, which sintered after the gels had collapsed.

III. PUBLICATIONS, MANUSCRIPTS, THESES, AND PRESENTATIONS

A. Publications and Manuscripts

1) M. J. Haun, I. A. Cornejo, J. Collier, S. M. Landin, Y. Kim, and B. Houng, "Processing Techniques for Crystal Alignment in Lead Germanate Based Compositions," Proceedings of the Sixth U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Maui, HI, Nov. 11-12, pp. 251-254 (1993).

2) S. M. Landin and M. J. Haun, "Solution-Derived Ferroelectrics in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ System," Ferroelectrics, 152, 91-96 (1994).

3) J. Collier, I. A. Cornejo, and M. J. Haun, "Ferroelectric Thick Films for Piezoelectric Applications," Ferroelectrics, 154, 47-52 (1994).

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7) S. M. Landin and M. J. Haun, "Processing and Characterization of Ferroelectric Thin Films in the $Pb_5Ge_3O_{11}$-$PbZr_{0.5}Ti_{0.5}O_3$ System," Proceedings of the Ninth IEEE International Symposium on the Applications of Ferroelectrics, The Pennsylvania State University, University Park, PA, IEEE Cat. No. 94CH3416-5, pp. 468-471 (1994).

8) Y. D. Kim, S. M. Landin, I. A. Cornejo, and M. J. Haun, "Low-Firing $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ - Pb5Ge2SiO11 Compositions for Thick-Film Capacitor Applications," Proceedings of the Ninth IEEE International Symposium on the Applications of Ferroelectrics, The Pennsylvania State University, University Park, PA, IEEE Cat. No. 94CH3416-5, pp. 585-588 (1994).

9) I. A. Cornejo, G. Sylvester, and M. J. Haun, "Ferroelectric Glass-Ceramics Based on $Pb_5Ge_3O_{11}$," Proceedings of the II Materials Science Symposium Franco-Chileno, Nov. 3 (1995).

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11) I. A. Cornejo and M. J. Haun, "Electrical Properties of $Pb_5Ge_3O_{11}$ - Based Ferroelectric Glass-Ceramic Compositions," Proceedings of the Materials Research Society 1995 Fall Meeting, Metastable Metal-Based Phases and Microstructures Symposium, paper E3.30, Boston, MA, Nov. 27 (1995).

12) I. A. Cornejo and M. J. Haun, "Thick Film Processing of $Pb_5Ge_3O_{11}$ - Based Ferroelectric Glass-Ceramic Compositions," Proceedings of the Materials Research Society 1995 Fall Meeting, Thermodynamics and Kinetics of Phase Transitions Symposium, paper C9.28, Boston, MA, Nov. 29 (1995).

13) M. J. Haun, I. A. Cornejo, Y. D. Kim, B. Houng, J. Collier, C. Y. Kim, S. M. Landin, W. H. Gemmill, "Ferroelectric Compositions for Thick Film Sensor, Actuator, and Capacitor Applications," Proceedings of the First Pan Pacific Microelectronics Symposium, Surface Mount Technology Association, Honolulu, HI, Feb. 6-8 (1996).

14) I. A. Cornejo and M. J. Haun, "Crystallization Behavior of Glass-Ceramics with Multiple Ferroelectric Phases, Part I: The $Pb_5Ge_3O_{11}$-$PbTiO_3$ System," submitted to *J. Mater. Res.*

15) I. A. Cornejo and M. J. Haun, "Crystallization Behavior of Glass-Ceramics with Multiple Ferroelectric Phases, Part II: The $Pb_5Ge_3O_{11}$-$PbZr_{1/2}Ti_{1/2}O_3$ System," submitted to *J. Mater. Res.*

16) B. Houng and M. J. Haun, "Densification, Crystallization, and Electrical Properties of Lead Zirconate Titanate Based Glass-Ceramics," submitted to *J. Am. Ceram. Soc.*

17) Y. D. Kim and M. J. Haun, "Low-Firing Ferroelectric Compositions for Capacitor Applications," submitted to *J. Am. Ceram. Soc.*

18) I. A. Cornejo and M. J. Haun, "Water Induced Crystallization of Melt-Derived $Pb_5Ge_3O_{11}$ Based Amorphous Compositions," submitted to *J. Mater. Res.*

19) B. Houng and M. J. Haun, "Effect of Additives and Zr/Ti Ratio on the Properties of Lead Zirconate Titanate Glass-Ceramics: I, Crystallization and Densification Behavior ," submitted to *J. Am. Ceram. Soc.*

20) B. Houng and M. J. Haun, "Effect of Additives and Zr/Ti Ratio on the Properties of Lead Zirconate Titanate Glass-Ceramics: II, Electrical Properties," to be submitted for publication.

21) S. M. Landin and M. J. Haun, "Ferroelectric Thin Films in the $Pb_5Ge_3O_{11}$ and $Pb_5Ge_3O_{11}$-$PbZr_xTi_{1-x}O_3$ Systems," to be submitted for publication.

22) W. H. Gemmill and M. J. Haun, "Sol-Gel Derived PZT with Additions of Silica and Lead Silicate," to be submitted for publication.

23) C. Y. Kim and M. J. Haun, "Transient Glass Phase Processing of Lead Zirconate Titanate Ceramics," to be submitted for publication.

24) Y. D. Kim abd M. J. Haun, "Lead Zinc Niobate Glass-Ceramics," to be submitted for publication.

B. Theses

1) James Collier, "Ferroelectric Thick-Films for Piezoelectric Applications Produced from Amorphous $Pb_5Ge_2SiO_{11}$ and Crystalline Pb(Zr,Ti)O3," M.S. Thesis No. T-4479, January 1994.

2) Yangdo Kim, "Low-Firing $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ - $Pb_5Ge_2SiO_{11}$ Compositions for Thick-Film Capacitor Applications," M.S. Thesis No. T-4515, June 1994.

3) Ivan A. Cornejo, "Low Temperature Crystallization of $Pb_5Ge_3O_{11}$ - $PbTiO_3$ and $Pb_5Ge_3O_{11}$ - $Pb(Zr_{1/2}Ti_{1/2})O_3$ Glass-Ceramic Systems with Multiple Ferroelectric Phases for Pyroelectric Applications," Ph.D. Thesis No. T-4631, July 1994.

4) Boen Houng, "Lead Titanate and Lead Zirconate Titanate Ferroelectric Glass-Ceramics,"Ph.D. Thesis, March 1996.

5) Steven M. Landin, "Ferroelectric Thin Films in the $Pb_5Ge_3O_{11}$ and $Pb_5Ge_3O_{11}$-$PbZr_xTi_{1-x}O_3$ Systems," Ph.D. Thesis, March 1996.

6) William H. Gemmill, "Sol-Gel Derived PZT with Additions of Silica and Lead Silicate," M.S. Thesis No. T-4882, May 1996.

7) Chan Young Kim, "Transient Glass Phase Processing of Lead Zirconate Titanate Ceramics," Ph.D. Thesis No. T-5010, June 1997.

8) Yangdo Kim, "Lead Zinc Niobate and Lead Magnesium Niobate Glass-Ceramics," Ph.D. Thesis, June 1997.

C. Presentations

1) I. A. Cornejo and M. J. Haun, "Ferroelectric Glass-Ceramics Based on the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ System," 94th Annual Meeting of the American Ceramic Society," Minneapolis, MN, April 14, 1992.

2) M. J. Haun, "Glass-Ceramics for Electronic Applications," ONR Transducer Materials Review, The Pennsylvania State University, State College, PA, April 22, 1992.

3) I. A. Cornejo and M. J. Haun, "Crystallization Behavior of $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ Ferroelectric Glass-Ceramics," 95th Annual Meeting of the American Ceramic Society, Cincinnati, OH, paper E-61-93, April 18-22, 1993.

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7) M. J. Haun, I. A. Cornejo, J. Collier, B. Houng, and S. M. Landin, "Crystallization and Microstructural Control of Ferroelectric Glass-Ceramics and Thin-Films," ONR Transducer Materials Review, The Pennsylvania State University, State College, PA, April 7, 1993.

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9) I. A. Cornejo, J. Collier, and M. J. Haun, "Ferroelectric and Crystallization Behavior in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ Glass-Ceramic System," 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993.

10) S. M. Landin and M. J. Haun, "Solution-Derived Ferroelectrics in the $Pb_5Ge_3O_{11}$-$PbTiO_3$-$PbZrO_3$ System," 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993.

11) B. Houng and M. J. Haun, "Lead Titanate and Lead Zirconate Titanate Piezoelectric Glass-Ceramics," 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993.

12) J. Collier, I. A. Cornejo, and M. J. Haun, "Ferroelectric Thick Films for Piezoelectric Applications," 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 8-13, 1993.

13) M. J. Haun, S. M. Landin, I. A. Cornejo, J. Collier, B. Houng, and Y. Kim, "Crystallization Behavior of Ferroelectric Thin-Films and Glass-Ceramics," PAC RIM Meeting, Honolulu, HI, November 7-10, 1993.

14) M. J. Haun, I. A. Cornejo, J. Collier, S. M. Landin, Y. Kim, and B. Houng, "Processing Techniques for Crystal Alignment in Lead Germanate Based Compositions," Sixth U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Maui, HI, Nov. 11-12, 1993.

15) M. J. Haun and B. Houng, "Piezoelectric Lead Zirconate Titanate based Glass-Ceramics," ONR Transducer Materials Review, The Pennsylvania State University, State College, PA, April 11-13, 1994.

16) I. A. Cornejo and M. J. Haun, "Low-Temperature Crystallization of Glass-Ceramics with Multiple Ferroelectric Phases," 96th Annual Meeting of the American Ceramic Society, Indianapolis, April 24-28, 1994.

17) B. Houng and M. J. Haun, "Piezoelectric Lead Zirconate Titanate based Glass-Ceramics," 96th Annual Meeting of the American Ceramic Society, Indianapolis, April 24-28, 1994.

18) Y. D. Kim and M. J. Haun, "Low-Firing $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$Pb_5Ge_2SiO_{11}$ Compositions for Thick-Film Capacitor Applications," 96th Annual Meeting of the American Ceramic Society, Indianapolis, April 24-28, 1994.

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25) B. Houng, C. Y. Kim, and M. J. Haun, "Piezoelectric Lead Zirconate Titanate - Lead Silicate Glass-Ceramics," Materials Research Society Fall Meeting, Boston, MA, Nov. 28, 1994.

26) B. Houng and M. J. Haun, "The Effect of Additives and Zr/Ti Ratio on the Properties of Lead Zirconate-Titanate Glass-Ceramics," American Ceramic Society 97th Annual Meeting, Cincinnati, OH, April 30 - May 4, 1995.

27) C. Y. Kim, B. Houng, and M. J. Haun, "Transient Glass Phase Processing of Lead Zirconate-Titanate Glass-Ceramics," American Ceramic Society 97th Annual Meeting in Cincinnati, OH, April 30 - May 4, 1995.

28) I. A. Cornejo, G. Sylvester, and M. J. Haun, "Ferroelectric Glass-Ceramics Based on $Pb_5Ge_3O_{11}$," II Materials Science Symposium Franco-Chileno, Nov. 3 (1995).

29) M. J. Haun, B. Houng, C. Y. Kim, and Y. D. Kim, "Piezoelectric Lead Zirconate Titanate Glass-Ceramics," Seventh U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Tsukuba, Japan, Nov. 14-17 (1995).

30) I. A. Cornejo and M. J. Haun, "Electrical Properties of $Pb_5Ge_3O_{11}$ - Based Ferroelectric Glass-Ceramic Compositions," Materials Research Society 1995 Fall Meeting, Metastable Metal-Based Phases and Microstructures Symposium, paper E3.30, Boston, MA, Nov. 27 (1995).

31) I. A. Cornejo and M. J. Haun, "Thick Film Processing of $Pb_5Ge_3O_{11}$ - Based Ferroelectric Glass-Ceramic Compositions," Materials Research Society 1995 Fall Meeting, Thermodynamics and Kinetics of Phase Transitions Symposium, paper C9.28, Boston, MA, Nov. 29 (1995).

32) M. J. Haun, I. A. Cornejo, Y. D. Kim, B. Houng, J. Collier, C. Y. Kim, S. M. Landin, W. H. Gemmill, "Ferroelectric Compositions for Thick Film Sensor, Actuator, and Capacitor Applications," First Pan Pacific Microelectronics Symposium, Surface Mount Technology Association, Honolulu, HI, Feb. 6-8 (1996).

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